

Heat Capacity of Polyisobutylene From 0° to 380° K¹

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Measurements of the heat capacity of polyisobutylene of the viscosity average molecular weight of 1.35×10^6 were made from about 14° to 380° K by means of an adiabatic calorimeter. The glass-transformation temperature was estimated to be 199° K. The values of the heat capacity above the glass-transformation temperature can be represented within ± 0.2 percent by

$$C(\text{abs j deg}^{-1} \text{ g}^{-1}) = 0.844 + 3.03 \times 10^{-3} T + 2.24 \times 10^{-6} T^2.$$

The data were used to obtain smoothed values of heat capacity, enthalpy, entropy, and Gibbs free energy from 0° to 380° K.

1. Introduction

This paper deals with one of a series of heat-capacity investigations on rubber polymers and related substances to obtain thermodynamic information. Ferry and Parks [1]² measured the heat capacity of polyisobutylene of an average molecular weight of about 4,900, as determined from cryoscopic measurements, in the range from 118° to 295° K. The heat-capacity measurements presented in this paper were made from about 14° to 380° K on a polyisobutylene sample of the viscosity average molecular weight of 1.35×10^6 . The results above the glass-transformation temperature (199° K) were found to be representable within ± 0.2 percent by a quadratic equation. The data were used to obtain a table of smoothed values of heat capacity, enthalpy, entropy, and Gibbs free energy from 0° to 380° K.

2. Apparatus and Method

The measurements of the heat capacity were made by means of an adiabatic calorimeter similar in design to that described by Southard and Brickwedde [2]. Details of the design and operation of the calorimeter and accessory apparatus have been given previously by Scott et al. [3]. Briefly, the experimental method was as follows: The polymer sample was sealed in a copper container provided with vanes to promote rapid dissipation of heat and with a central well for a platinum-resistance thermometer and heater assembly. The container was suspended within the evacuated adiabatic shield system which was maintained at the same temperature during the heat-capacity experiments as that of the sample container surface by controlling shield heaters, using multiple junction constantan-chromel-P thermocouples to integrate surface temperatures. The outer surface of the container and the adjacent shield surface were gold-plated and polished to minimize heat transfer by radiation. The vacuum surrounding the container and shield was 10^{-5} mm of Hg or better. The electric-power input to the calorimeter heater

(100 ohms) was measured by means of a Wenner potentiometer in conjunction with a volt box. The duration of each heating interval was measured with an interval timer operated on 60-cycle standard frequency furnished by the Radio Section of the Bureau. The timer was compared periodically with time signals from the Bureau's Time Section and was found to vary not more than 0.02 sec for a heating period that was never less than 2 min.

The temperature measurements were made by using a platinum-resistance thermometer in conjunction with a Mueller bridge. The thermometer was calibrated above 90° K in accordance with the 1948 International Temperature Scale [4], and between 10° and 90° K with a provisional scale [5], which consists of a set of platinum-resistance thermometers calibrated against a helium-gas thermometer. The provisional scale, as used in the calibration, was based on the value of 273.16° K for the temperature of the ice point and 90.19° K for the temperature of the oxygen point.

3. Sample

The polyisobutylene investigated was a portion of a larger sample designated as Vistanex B-100, which had been selected from a regular production run at the Esso Standard Oil Co. plant at Elizabeth, N. J. The molecular weights of this polymer determined from the average of intrinsic viscosities and from the light-scattering measurements have been reported by Marvin [6] to be, respectively,

$$M_v = 1.35 \times 10^6$$

and

$$M_w = 1.56 \times 10^6.$$

Information regarding other physical properties of this polymer sample can be found in the reference cited [6]. According to the analysis made by Esso Standard Oil Co., the sample contained 0.01 percent of ash and about 0.1 percent of paratertiarybutylcresol as stabilizer. The sample was used in the heat-capacity investigations without further treatment.

The polyisobutylene sample was cut, as in the previous heat-capacity studies of polymers [7,8,9], to fit between the vanes of the calorimeter sample

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² Figures in brackets indicate the literature references at the end of this paper.

container. After filling, the sample was pumped at high vacuum for several weeks to eliminate as much of the volatile impurities as possible. The sample (40.736 g) was finally sealed in the container, along with a small quantity of helium gas to permit rapid thermal equilibrium during the calorimetric experiments.

4. Results

The heat-capacity measurements were made from about 14° to 380° K. The experimental details concerning heat treatments, temperature range of the measurements, and temperature drifts are summarized in table 1. The observed values of the heat capacity are given in table 2 and plotted in figure 1. As in the previous heat-capacity studies of polymers of butadiene and styrene [7,8,9] the polyisobutylene sample was subjected to two different rates of cooling prior to the heat-capacity experiments in order to obtain information on how the heat capacity was dependent upon the thermal history. In one series of measurements, by immersing the calorimeter in liquid nitrogen with helium gas in the space surrounding the sample container, the polymer was cooled from room temperature to 90° K in about 30 min and to 80° K in an additional 30 min. By this procedure a large portion of the polymer molecules was expected to be "frozen" in the higher states of energy.

In the second series of experiments, the polymer was cooled slowly over several days by maintaining a high vacuum in the space surrounding the container

and by using different refrigerants successively. In the previous heat-capacity studies of polymers [7,9] that did not crystallize, the heat capacity in the region below the glass-transformation temperature seemed to be significantly dependent only upon the rate of cooling in the temperature range of the glass transformation. The polymer sample concerned in this investigation of the glass-transformation temperature 199° K, was cooled slowly only to 165° K and rapidly to lower temperatures (see table 1, run 5). The slow-cooling process was expected to allow more time for the polymer molecules to transform into states of lower energy.

TABLE 2. *Observed heat capacity of polyisobutylene, Vistanex B-100*
°K = °C + 273.16°

T	C	T	C
Run 1			
°K	abs $j \ deg^{-1}g^{-1}$	°K	abs $j \ deg^{-1}g^{-1}$
53.71	0.2627	242.80	1.711
54.55	.2679	252.99	1.752
56.22	.2773	263.00	1.794
59.16	.2941	272.88	1.838
62.68	.3146	282.59	1.878
65.85	.3336	292.23	1.920
69.35	.3545	302.85	1.968
73.59	.3804	314.27	2.019
78.06	.4091	325.56	2.070
82.65	.4390		
87.35	.4706		
Run 4—Continued			
147.46	0.8404		
156.18	.8939		
165.28	.9149		
174.52	1.006		
184.02	1.032		
191.06	1.142		
195.63	1.228		
199.98	1.430		
204.60	1.578		
209.43	1.630		
215.78	1.627		
Run 5			
14.43	0.0502		
15.71	.0579		
17.15	.0663		
18.66	.0753		
20.11	.0838		
21.76	.0935		
23.65	.1045		
25.58	.1156		
27.53	.1262		
29.75	.1383		
32.40	.1526		
35.48	.1688		
38.80	.1856		
42.50	.2044		
46.33	.2242		
50.16	.2445		
54.92	.2700		
60.03	.2991		
Run 6			
210.28	1.513		
216.45	1.604		
Run 7			
331.06	2.097		
341.38	2.142		
351.47	2.188		
Run 8			
305.21	1.981		
314.42	2.021		
Run 9			
325.41	2.072		
346.24	2.166		
366.68	2.257		
377.14	2.301		
Run 10			
310.59	2.004		
321.39	2.054		

TABLE 1. *Heat treatments and observations with polyisobutylene, Vistanex B-100*

Run	Treatment of sample	Temperature range of measurements	Temperature drift observations
1...	Cooled slowly to 80°, then rapidly to 53° K.	53 to 89-----	No drift.
2...	Cooled slowly to 80°, then rapidly to 14° K.	14 to 62-----	Do.
3...	Cooled rapidly from room temperature to 81° K.	81 to 218-----	Upward drift from 144° to 199°. Downward drift from 205° to 218°.
4...	Cooled rapidly from room temperature to 205° K and heated to 213° K.	213 to 331-----	No drift.
5...	Cooled slowly from room temperature to 165° K in 4 days. Cooled rapidly to 136° K, and heated to 143° K.	143 to 220-----	Downward drift from 160° to 220°.
6...	Cooled slowly from 220° to 180° K, and heated to 208° K.	208 to 220-----	Downward drift from 208° to 220°.
7...	Cooled slowly from 100° C to room temperature.	325 to 355-----	No drift.
8...	Left at room temperature over night.	300 to 320-----	Do.
9...	Left at room temperature for 2 days.	320 to 380-----	Do.
10...	Cooled slowly to 300° C	300 to 330-----	Do.

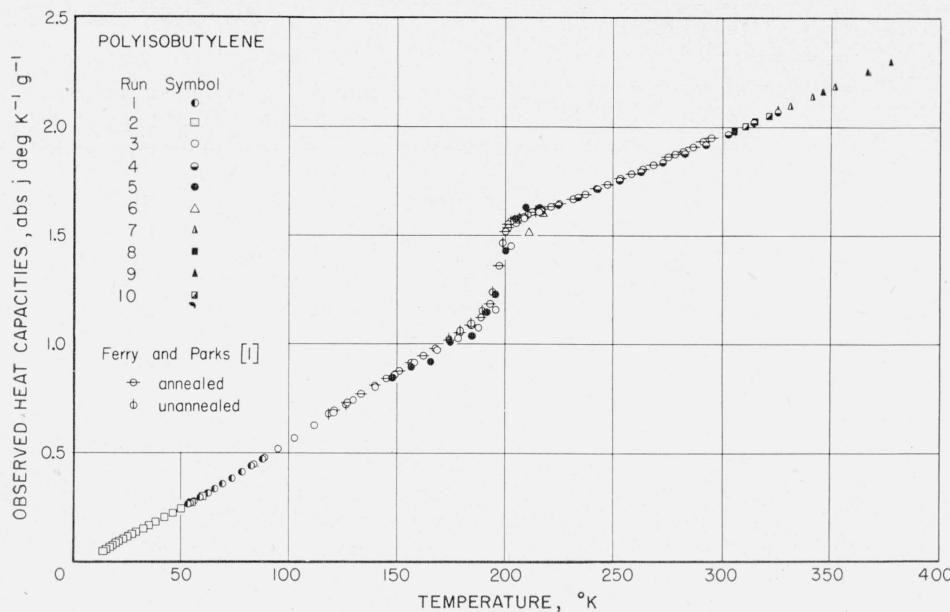


FIGURE 1. *Observed heat capacities of polyisobutylene.*

The measurements of run 3, with the sample shock-cooled, showed upward temperature drifts from about 144° to 199° K and downward drifts from about 205° to 219° K. The results of runs 5 and 6, made with the sample slowly cooled, showed downward temperature drifts from 160° to 220° K. It seems from these results that downward temperature drifts occurred in the temperature range from about 205° to 220° K, regardless of previous heat treatment. In run 4, however, when the sample was cooled rapidly from room temperature to 205° K and heated to 213° K, no drifts were observed in this range. Downward temperature drifts have been observed above the glass-transformation temperature with polymers that crystallize [7,8]. As the polymer melted slowly at certain temperatures above the glass-transformation temperature, heat was absorbed accompanied by downward temperature drifts. The downward temperature drifts from about 205° to 220° K observed with this polymer, however, are probably associated with glass transformation.

During the initial measurements, the temperature drifts in the region of the glass-transformation temperature were followed for several hours. The results indicated that temperature equilibrium would not be attained within a reasonable length of time. Similar observations were made during heat-capacity measurements on other polymers [7,8,9]. Consequently no attempt was made in subsequent measurements on the polymer to reach temperature equilibrium in the region of the glass-transformation temperature. However, any reasonable change in the time intervals used is considered not to alter the general nature of the heat-capacity results obtained.

The values of the heat capacity, in the region (210°

to 380° K) above the glass-transformation temperature can be represented within ± 0.2 percent (the average deviation being 0.1 percent) by the quadratic equation

$$C(\text{abs j deg}^{-1} \text{g}^{-1}) = 0.844 + 3.03 \times 10^{-3} T + 2.24 \times 10^{-6} T^2.$$

The constants were obtained by the method of least squares. Although the deviation of the observed heat-capacity values from this equation shows a small systematic trend, no attempt was made to obtain a better equation.

The heat-capacity data were used to obtain smoothed values of heat capacity, from which were derived the values, relative to 0° K, of enthalpy, entropy, and Gibbs free energy given in table 3. The values of the heat capacity below 14° K were obtained by extrapolation, using a Debye function fitted to the experimental values in the lowest temperature range. The method by which the derived thermal properties were obtained from the values of smoothed heat capacity has been described previously [7].

Upon consideration of various sources of errors, such as reproducibility of the physical state of the polymer, energy input, heat leak, and thermometry, the uncertainty in the heat-capacity values given in tables 2 and 3, except in the vicinity of the glass-transformation temperature and below 90° K, was estimated to be 0.3 percent. Below 90° K the uncertainty increases to 1 percent at 14° K. The uncertainty in the values of enthalpy, entropy, and Gibbs free energy, relative to 0° K, derived from the heat capacity was estimated to be 0.3 to 0.4 percent.

TABLE 3. Heat capacity, enthalpy, entropy, and Gibbs free energy of polyisobutylene, Vistanex B-100

T	C	(H _T - H _{0°K})	(S _T - S _{0°K})	-(F _T - F _{0°K})
°K	abs j deg ⁻¹ g ⁻¹	abs j g ⁻¹	abs j deg ⁻¹ g ⁻¹	abs j g ⁻¹
0	0	0	0	0
5	0.0023	0.0015	0.0007	0.0019
10	.0180	.0453	.0061	.0153
15	.0536	.2215	.0197	.0734
20	.0831	.5645	.0393	.2210
25	.1123	1.053	.0610	.4710
30	.1397	1.684	.0839	.8331
35	.1663	2.449	.1074	1.311
40	.1918	3.345	.1313	1.908
45	.2177	4.368	.1554	2.625
50	.2439	5.522	.1797	3.463
55	.2705	6.808	.2042	4.423
60	.2990	8.231	.2289	5.505
65	.3283	9.799	.2540	6.712
70	.3583	11.52	.2794	8.046
75	.3895	13.38	.3052	9.507
80	.4215	15.41	.3314	10.99
85	.4544	17.60	.3579	12.82
90	.4872	19.95	.3848	14.68
95	.5196	22.47	.4120	16.67
100	.5520	25.15	.4395	18.80
105	.5842	27.99	.4672	21.07
110	.6163	30.99	.4951	23.47
115	.6483	34.15	.5232	26.02
120	.6802	37.48	.5515	28.70
125	.7122	40.96	.5799	31.53
130	.7436	44.60	.6085	34.50
135	.7748	48.39	.6071	37.62
140	.8056	52.34	.6658	40.87
145	.8361	56.45	.6946	44.28
150	.8660	60.70	.7235	47.82
155	.8950	65.11	.7524	51.51
160	.9236	69.65	.7812	55.34
165	.9522	74.34	.8101	59.32
170	.9804	79.17	.8389	63.45
175	1.008	84.15	.8677	67.71
180	1.035	89.26	.8965	72.12
185	a 1.06	-----	-----	-----
190	1.10	-----	-----	-----
195	1.18	-----	-----	-----
200	a 1.42	-----	-----	-----
205	1.54	-----	-----	-----
210	1.58	-----	-----	-----
215	1.60	-----	-----	-----
220	1.620	144.0	1.163	113.1
225	1.640	152.2	1.205	118.9
230	1.661	160.4	1.241	125.1
235	1.681	168.8	1.277	131.4
240	1.702	177.2	1.313	137.9
245	1.722	185.8	1.348	144.5
250	1.743	194.5	1.383	151.3
255	1.764	203.2	1.418	158.3
260	1.785	212.1	1.452	165.5
265	1.806	221.1	1.486	172.8
270	1.827	230.2	1.520	180.4
273.16	1.840	235.9	1.542	185.2
275	1.848	239.3	1.554	188.1
280	1.870	248.6	1.588	195.9
285	1.891	258.0	1.621	203.9
290	1.913	267.5	1.654	212.1
295	1.934	277.2	1.687	220.5
298.16	1.948	283.3	1.708	225.8
300	1.956	286.9	1.720	229.0
305	1.978	296.7	1.752	237.7
310	2.000	306.7	1.784	246.5
315	2.022	316.7	1.817	255.5
320	2.045	326.9	1.849	264.7
325	2.067	337.2	1.880	274.0
330	2.090	347.6	1.912	283.5
335	2.112	358.1	1.944	293.1
340	2.135	368.7	1.975	302.9
345	2.158	379.4	2.007	312.9
350	2.181	390.3	2.038	323.0
355	2.204	401.2	2.069	333.3
360	2.227	412.3	2.100	343.7
365	2.250	423.5	2.131	354.2
370	2.274	434.8	2.162	365.0
375	2.297	446.2	2.192	375.8
380	2.321	457.8	2.223	386.9

* The values between 185° and 215° K, inclusive, were obtained graphically from the best curve drawn through the observed heat capacities.

5. Discussion

Ferry and Parks [1] previously determined the heat capacity of polyisobutylene of the number-average molecular weight of 4,900 from 118° to 295° K. Their results (see fig. 1) are generally about 1 to 2 percent higher than those obtained in the present investigation on a polyisobutylene sample of the viscosity average molecular weight of 1.35×10^6 . The glass-transformation temperature (197° K) reported by Ferry and Parks is essentially the same as that (199° K) estimated from the results of the present measurements, the transformation temperature being taken as the temperature at the "half-height" of the upward sweep in heat capacity. The sharp decrease in heat capacity at the glass-transformation temperature was estimated to be about 26 percent. This percentage decrease is similar to those found in other polymers previously investigated [7, 8, 9].

The temperature drifts observed (see table 1), in the region of the glass-transformation temperature and immediately below, were similar to those of polymers previously investigated [7, 8, 9]. The discussion regarding these temperature drifts that are associated with glass transformation can be found in the references cited [7, 8, 9].

When the polymer sample was previously cooled rapidly (run 3), the enthalpy change obtained between 180° and 220° K was 53.27 abs j g⁻¹; when cooled slowly (run 5), the enthalpy change was 54.77 abs j g⁻¹. The difference indicates qualitatively the degree of the relaxation effects associated with glass transformation under the conditions of the experiments discussed. In a previous investigation [9], the enthalpy changes between 195° and 225° K, obtained under similar experimental conditions on a butadiene-styrene copolymer containing 22.61 weight percent of bound styrene, were 40.39 and 41.95 abs j g⁻¹ when the sample was rapidly and slowly cooled, respectively.

6. References

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